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Field Emission from Acid Treated Diamond Films *

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A stable electron emission was obtained at as low as about 2.5 V/μm from acid treated diamond films. The emission data were fitted with Folwer-Nordheim theory. It is found that the non-electrons are emitted from some protrusions on surface of diamond films, and that after acid treatment, the effective work function is lowered, and the emission area is increased to two folds of those of as-grown films. These results were discussed.

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Recently chemical vapor deposition diamond films have attracted much attention as a potential cathode materials, due to their excellent physical and chemical properties such as chemical inertness, high thermal conductivity and negative electron affinity etc. But field emission from diamond films shows complex properties. For example, some report field emission following Folwer-Nordheim (F-N) theory,[1] while others did not;[2] Geis reported that a high emission could be obtained at lower electrical field after surface treatment and doping.[3] The electron transport process in field emission from the diamond films is very important in understanding the field emission properties, and several models have been suggested such as by defect[4] and impurities,[5] by "hot" electron[6] or break down,[7] and others.[8] Surface treatment such as acid-treatment on thin films is a way to observe the electron transport process and to obtain a higher emission by changing the surface morphology. In this paper the effect of acid treatment was studied.

The diamond films were prepared on n-type silicon wafers by the microwave plasma chemical vapor deposition technique with the following conditions: microwave power 500 W; substrates temperature 900°C; the ratio of hydrogen vs methane 100 : 2. The deposition lasts 1 h to prepare thin films about 0.3 μm thickness. Before deposition the silicon wafers were abraded with diamond powder 50 μm in diameter for 10 min. The deposited films were treated with a mixture of sulfuric acid and nitric acid at about 150°C for 15 min, then washed with deionized water. The field emission was measured in a high vacuum system at 10^{-8} Torr. The distance between cathode and anode was 120 μm.

Figure 1 shows the field emission current−voltage plots. It shows that the field emission from diamond films is significantly increased after acid treatment, and that the turn-on voltage is reduced. The emission data were fitted with F-N theory and shown in Fig. 2 by solid lines.

Figure 2 was the emission stability plots, it shows that emission current from acid treated films is more stable than that of as-deposited.

Atomic force microscopy study[9] shows that a continuous film of about 0.3 μm thickness is formed, and that there are many protrusions distributed on the surface. Especially after acid treatment the number of protrusions increased in one or two orders compared with that of as-deposited films, and the protrusions were sharpen, also distributed more uniformly on the surface. A thin film is necessary to investigating the effect of acid treatment on field emission. x-ray diffraction study shows that the films were mainly (111) oriented, and that narrower full width at half of maximum appeared in the acid treated films.

According to the F-N theory, the emission current vs voltage applied for field emission can be written in following form:

$$I = aV^2 \mathrm{e}^{-b/V}, \tag{1}$$

$$a = c_1 \frac{A}{E_\varphi} \mathrm{e}^{10.4/E_\varphi^{1/2}} \beta^2, \quad b \approx c_2 E_\varphi^{3/2} \beta^{-1}, \tag{2}$$

where c_1 and c_2 are constants, E_φ is the work function, A and β are the emission area or effective area, and the factor of field enhancement, respectively. The values of a and b could be got from fitting the emission data with F-N theory, and are given in Fig. 1.

Acid treatment will influence the surface morphology of the diamond films. Usually because of the effect of electrical field enhancement on a sharp protrusion, electron could be more easily emitted from these sites. After acid treatment, the protrusions are far sharper than those of as-deposited films, and the value b, which

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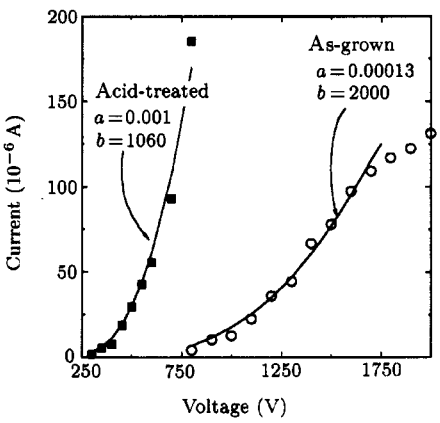

Fig. 1. Field emission plots fitted with F-N theory by the solid lines.

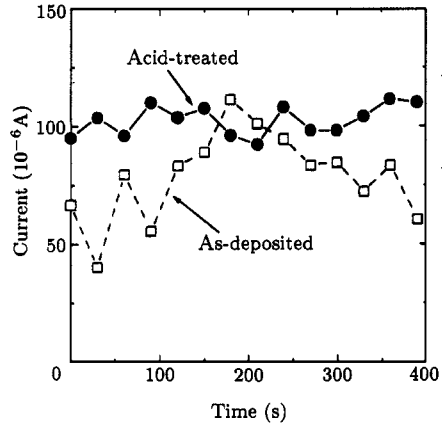

Fig. 2. Emission stability plots.

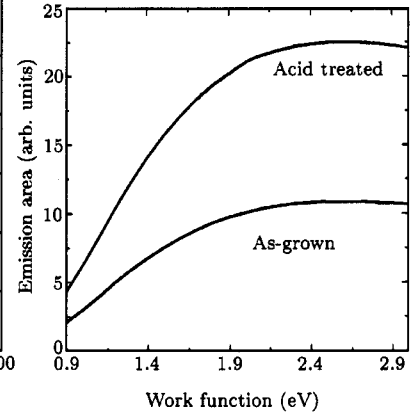

Fig. 3. Plots of emission area vs the work function of the diamond films.

relates to the effective work function, is about half of that of as-deposited film (β_{as}/β_{acid} = 1060/2000 = 0.53). So the turn-on voltage was reduced. But the value b is lower than that expected. The number of protrusions is more than that of as-grown sample by one or two orders, but the emission sites are about two folds of those of as-grown films, i.e.

$$\frac{A_{acid}}{A_{as}} = \frac{0.001 \times (1060)^2}{0.00013 \times (2000)^2} \approx 2.2,$$

if there is no-change in work function after acid treatment. It is difficult to compare the emission sites and work function between these samples, when there is an obvious influence on the work function after acid treatment. While the emission sites A vs E_φ could be plotted from Eq. (2) and are given in Fig. 3. If supposing that the emission sites are ten folds of those of as-grown films and the work function of as-grown film is about 0.9 eV, the work function after acid treatment is about 2.0 eV. In other words, many protrusions are not the sites where the electrons were emitted. Probably besides the increase of work function, there is also a lower field enhancement on some protrusions caused by two reasons: one is the higher density of protrusions, the other is the low electric conductivity of the diamond films. The stable emission from acid treated film is due to the increase of the number of protrusions, and relatively more emission sites.

Especially after acid treatment, the impurities such as graphite and amorphous carbon on the surface and/or in the interface between diamond grains will be etched away (because of the thin films). Therefore it is impossible that the emitted electrons were transported by these impurities. Some researchers reported that the graphite or impurities in the films plays a role in electron transport process in the field emission. But the emission from as-grown films shows saturation at higher field region, while a high emission was obtained after acid treatment. The impurities on the surface and/or in the interface between the grains are not favorable to electron transport, and electron transport process in field emission is complex. Probably the defect in the films plays an important role in electron transport process.

It has been reported that there is a nonuniform emission from diamond films[6] and that the emission sites increase with the applied electrical field.[10] Probably it is due to a nonuniform distribution and sharpness of the protrusions. For sharp protrusions the electrons can be emitted at lower voltage, while higher voltage is necessary for a dull protrusions.

In summary, acid treatment is a way to obtain a high emission at low field region. There are many protrusions on the surface of diamond films, and by acid treatment, the protrusions can be sharpen and their number increased, but there are no-electrons emitted from protrusions. The electron transport process in field emission from diamond films is complex, and the defect in the films maybe plays an important role.

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